

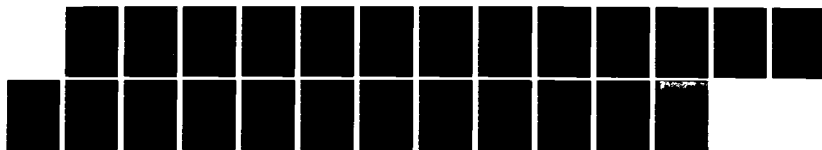
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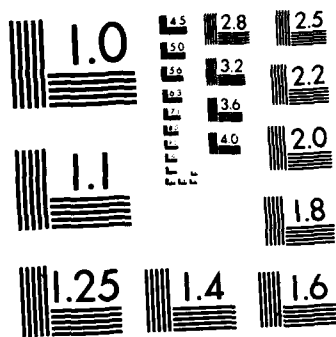
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BY

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Prepared for Publication in the Journal of Physical Chemistry

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# ABSTRACT

The coaxial translational time of flight (TOF) distributions of CS radicals produced in the 193nm laser photolysis of CS<sub>2</sub> have been measured. The population of CS with low translational energy is higher in the coaxial TOF measurements than it is with perpendicular measurements. These distributions have been analyzed using the Kresin-Lester adiabatic theory of photodissociation to obtain an upper limit for the S(<sup>3</sup>P)/S(<sup>1</sup>D) branching ratio of 2.1. If this analysis is correct it also suggests that significant amounts of CS radicals are produced in vibrational levels as high as v''=12 and that there are angular momentum constraints in the photodissociation process.

## INTRODUCTION

The photolysis of  $\text{CS}_2$  in the 180 to 210 nm region has been investigated by a number of workers (1,2,3,4,5) using various techniques including laser induced fluorescence (3), atomic resonance fluorescence (2), and velocity measurement of the fragments (1). Despite the multitude of studies there is still some controversy with respect to the branching ratio between the channels that produce  $\text{S}^1\text{D}$  and  $\text{S}^3\text{P}$ . In particular it has been suggested that the formation of  $\text{S}^3\text{P}$  (4,5) is the dominant channel, while Yang et.al. (1) suggest that the  $\text{S}^1\text{D}$  is dominant. The latter authors argue that very rapid quenching of  $\text{S}^1\text{D}$  by  $\text{CS}_2$  is the reason that the other techniques detected mostly  $\text{S}^3\text{P}$ . On the other hand, since Yang et.al. (1) measured the time of flights of the fragments using a perpendicular laboratory geometry there is an experimental bias against fragments with velocities lower than the beam velocity since these can never reach the detector. In the present work we will describe experiments where the time of flight of the fragment is detected coaxially with the beam. In this manner we are able to measure those low energy fragments that can escape detection in the perpendicular arrangement.

## EXPERIMENTAL

A schematic diagram of the apparatus is shown in Figure 1. It consists of a pulsed valve source which produces a molecular beam that is crossed 2cm downstream by an ArF laser beam produced by a Lambda Physik EMG 101 excimer laser. The pulsed beam and the



fragments are passed through a skimmer, through the buffer chamber, into a detector chamber, and an ionizer of a quadrupole mass spectrometer. The ionizer is 13.4 cm downstream from the interaction region where the laser and the molecular beam cross each other. The first chamber and the buffer chamber are both pumped by liquid nitrogen trapped six inch diffusion pumps, while the mass spectrometer chamber is pumped by an ion pump along with a titanium getter pump. With this arrangement we are able to obtain pressures of  $5 \text{ to } 6 \times 10^{-8}$  torr in the mass spectrometer chamber with the beam on. Even so, there is still considerable background noise at both the CS and S masses from  $\text{CS}_2$  in the beam which undergoes dissociative ionization in the ionizer. To overcome this noise two techniques have been employed. First, the electron energy is lowered to 15 eV to reduce the amount of interference that comes from dissociative ionization of carbon disulfide. Second, the experiment is carried out by pulsing the molecular beam at twice the rate of the laser beam, and counting up in the multichannel analyzer when both the molecular beam and the laser are on, and down when the laser beam is off.

A typical time of flight spectrum is shown in Figure 2. This spectrum exhibits a signal to noise ratio of about 5, which was obtained after 15000 laser shots. The center of mass beam velocity can be determined by measuring the decrease in the  $\text{CS}_2^+$  parent peak as a result of the laser photolysis. The time of flight for the ions observed in this study inside the quadrupole was determined by sharply pulsing the extractor electrode and then measuring the time it takes for these ions to reach the electron multiplier.

## RESULTS AND DISCUSSION

The measured TOF distributions can be converted to translational energy distributions using the measured beam velocity and time of flight of the ions. These translational energy distributions are shown in Figure 3 along with one from Yang et.al.(1), and one taken in our apparatus for the perpendicular arrangement. In the latter case a single experiment was done to be sure that our apparatus could reproduce their previous result (1). It is clear from Figure 3 that both beam machines yield consistent data. Because of the very poor signal to noise ratio in the perpendicular arrangement in our apparatus the results of Yang et.al. (1) were used in the analysis of the high translational energy regime. It should be noted that the perpendicular geometry has an intrinsically higher resolution at these energies than the coaxial geometry. The two sets of results for the perpendicular geometry curve over at different translational energies. This behavior is a reflection of the different beam velocities that are used in the experiments and further confirms that such a geometry will underestimate the fraction of low velocity fragments produced in the experiment.

The high energy break described by Yang et.al. (1) is more clearly seen in the perpendicular geometry because of it's higher resolution. This high energy break has been ascribed by them to the onset of the  $S(^1D)$  channel in the photodissociation process. We agree with this interpretation since, as they pointed out, it occurs at the correct energy for this

process and the analysis (6) of the spectrum at longer wavelengths indicates that there is some mixing of the singlet with the triplet state. This has been further confirmed by a recent report of an analysis of the absorption spectra (7) of CS<sub>2</sub> in pulsed molecular beams in the region around 200nm.

Even though this break probably does correspond to the onset of the production of S(<sup>1</sup>D) it is not clear just how the fraction due to S(<sup>3</sup>P) can be separated from the fraction due to S(<sup>1</sup>D). One way is to follow the earlier procedure (1) and assign all of those molecules with translational energies higher than the break to S(<sup>3</sup>P), and all those with translational energies lower than the break to S(<sup>1</sup>D). This of course gives a lower limit to the amount of triplet P atoms produced, but the procedure has little justification. An alternate method would be to appeal to theory as a means of unravelling these two distributions.

Kresin and Lester (8,9,10,11) have recently published an adiabatic theory of photodissociation that can be used to unravel these two distributions. The theory can be used to derive an expression for the probability,  $P(i,v'')$ , that a S atom in the  $i$ th state will be accompanied by a CS radical in the  $v''$  level is given by,

$$P(i,v'') = K(i)\exp(C(E_{\text{trans}}/E_{\text{vib}})v'') \quad (1.)$$

The value of  $C$ , can be calculated using the vibrational frequencies of the excited state of CS<sub>2</sub> and the ground state of CS. Recent measurements (7) of the absorption spectra show that even though the excited state of CS<sub>2</sub> is bent, the absorp-

tion at 193nm leads to a quasi-linear excited state. The symmetric frequency of this state is  $392\text{cm}^{-1}$ . Nothing is known about the asymmetric frequency, but assuming that it has decreased to about  $1000\text{cm}^{-1}$  because of the decrease in bonding one can calculate a value of  $C$  of about 2.. By taking the observed probabilities for the translational energies from 18 to 38 Kcal/mol corresponding to the production of only  $S(^3P)$  and transforming these into the probability for a given vibrational quantum number we obtain the results shown in Figure 4. Extrapolating this curve out to  $v''=12$ , the probability distribution curve for the  $S(^3P)$  is obtained. This probability curve can be combined with the observed curve to obtain the probability curve for  $S(^1D)$  atoms which is also shown in Figure 4.

By summing these probability distributions, one can calculate the  $S(^3P)/S(^1D)$  branching ratio at this wavelength. The derived branching ratio is 2.1:1, which can be considered an upper limit. This is considerably larger than the ratio of 0.25:1 computed by Yang (1) but as Table 1 shows they would have obtained an even larger ratio of 5.6:1 if they had used the present method. A branching ratio this large for the production of  $^3P$  to  $^1D$  sulfur atoms implies that spin conservation is not important in this particular dissociation process. Since the ground state of  $\text{CS}_2$  is a singlet, the triplet sulfur atoms must be produced by the upper excited state crossing over to a triplet state before or during dissociation. Evidently the sulfur atom is large enough that spin-orbit interaction breaks the selection rule that prevents a change in the multiplicity

during a transition. A similar conclusion was reached earlier (4,5) using methods that are entirely different from those used in these experiments. It is important to reiterate that the present experimental results demonstrate that a substantial fraction of the CS radicals are produced with low translational velocities and would not be detected in a perpendicular arrangement. Thus, despite which method is used to separate the two channels, the coaxial arrangement will result in the detection of a higher fraction of  $S(^1D)$  atoms.

In addition to obtaining branching ratios the probability curves can also be used to obtain the value of the ratio  $f_c = E_{trans}/E_{vib}$  for the two channels. The values of this ratio that are obtained are 0.09 and 0.3 for the triplet P and singlet D sulfur atoms channels respectively. In both cases this ratio is less than one which states that more energy goes into the vibrational degrees of freedom than into the translational recoil energy between the two fragments. Thus, in the triplet P atom 10 times as much energy appears in vibration as compared to translation while in the singlet D atom slightly less than 3 times as much energy appears in vibration. Evidently in the latter case some of the energy that would have gone into vibration has appeared as electronic excitation of the sulfur.

The analysis of the data using the theory as a guide has suggested that the CS fragment that is produced together with  $S(^3P)$  should have a great deal of vibrational energy. Yet when laser induced fluorescence studies (3) are used to measure the quantum state distribution of the fragments, no evidence is found for vibrational levels above  $v''=6$ . However, in the parti-

cular vibrational sequence used the Franck-Condon factors were rapidly decreasing for transitions from the expected higher vibrational levels of the ground state. Because of this, different regions of the spectra have to be probed if these upper vibrational levels are to be detected.<sup>12</sup> In principle the flash photolysis kinetic absorption studies (4) should have been able to detect the higher vibrational levels but the studies were done at very high pressures, and with flash lamps with a large pulse width. Both of these factors could have precluded the detection of the upper vibrational states.

In all of the above discussion no account has been taken of the rotational distribution of the CS fragment. The justification for this is that the measured rotational distribution (3) suggest that only 2 to 2.5 Kcal/mole of the 45 Kcal/mole of available energy goes into internal rotational excitation of the fragment. An examination of the curves of the  $\ln$  of the probability versus the vibrational quantum number shows that the curves roll off at low vibrational quantum numbers. This can possibly be explained by invoking an angular momentum constraint in the photodissociation process. It is known that the upper state of CS<sub>2</sub> is bent (6,7) so that some of the excess energy must go into rotation of the fragment even though the molecule is quasi-linear when it is excited. If the amount of the energy that goes into rotation is constrained by conservation of angular momentum and the translational recoil is constrained by the repulsive force at low vibrational levels, the probability for producing these low levels will be lower since progressively fewer and fewer molecules will have the necessary energy to meet both conditions.

## CONCLUSIONS

The coaxial and perpendicular time of flight distributions for the CS fragment have been analyzed using the adiabatic photodissociation theory (8). The results indicate that the branching ratio for the triplet to singlet channel is about 2:1. This is in agreement with earlier results obtained using both the kinetic absorption flash photolysis method (4) and product analysis (5). Most of the available energy appears to go into internal energy of the CS fragment and there appears to be a strong angular momentum constraint on the photodissociation process. The analysis suggests that CS radicals should be formed in vibrational levels up to  $v''=13$ , and work is currently underway to determine whether this is the case. Finally, the coaxial time of flight arrangement has been shown capable of detecting fragments that are produced with low translational recoil energies in the center of mass system.

#### ACKNOWLEDGEMENTS

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TABLE 1

BRANCHING RATIO OF TRIPLET P AND SINGLET D SULFUR ATOMS

-----		
[ <sup>3</sup> P]/[ <sup>1</sup> D]		
-----LOWER LIMIT*-----UPPER LIMIT**--		
THIS WORK	0.18	2.1
-----		
YANG et.al.(1)	0.25	5.6
-----		

\* Using the method of Yang et.al. to determine this ratio.

\*\* Using the method described in this paper to determine the ratio.

### Figure Captions

- Figure 1. Schematic of molecular beam photolysis apparatus for TOF measurement on coaxial geometry.
- Figure 2. A typical TOF spectrum of CS fragments on coaxial geometry.
- Figure 3. Translational energy distribution of photo-fragmentation of CS<sub>2</sub> 193nm from conversion of TOF spectra. Comparison of the results of coaxial to perpendicular detection is shown: (●)----From coaxial detection averaged over 5 measurements; (○)----from Yang, et.al. [1]; and (□)----one measurement at right angle in this work. There is a break that occurs at  $E_T = 18$  Kcal/mol. The error bars refer to the coaxial detection arrangement.
- Figure 4. Inferred vibrational population of CS<sub>2</sub> fragments produced in processes: (a). CS<sub>2</sub> +  $h\nu$  → CS ( $X^1\Sigma, v''$ ) + S (<sup>3</sup>P) represented by ○; (b). CS<sub>2</sub> +  $h\nu$  → CS ( $X^1\Sigma^+, v''$ ) + S (<sup>1</sup>D) represented by ●

# SCHEMATIC OF TIME-OF-FLIGHT APPARATUS

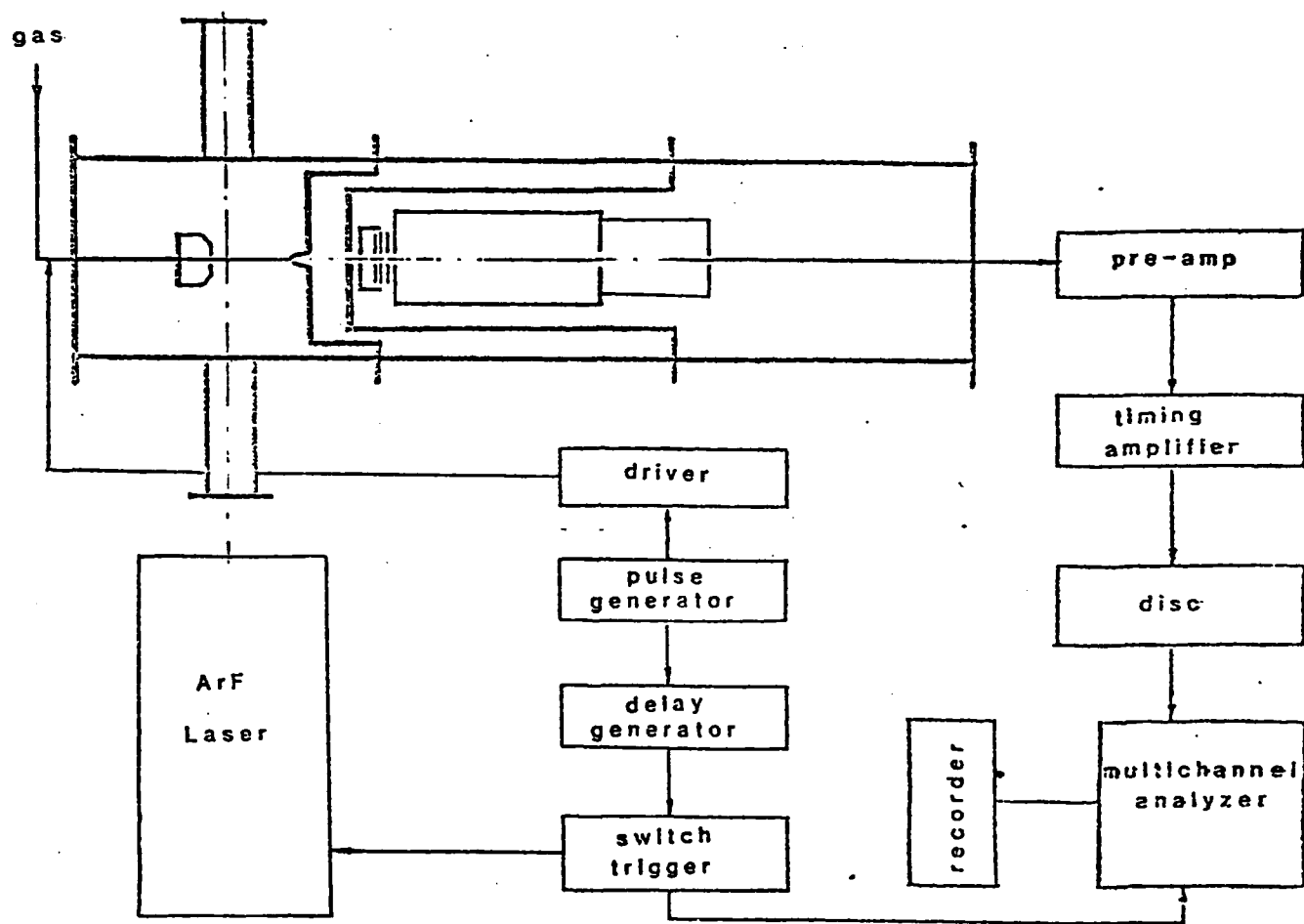


FIGURE 1

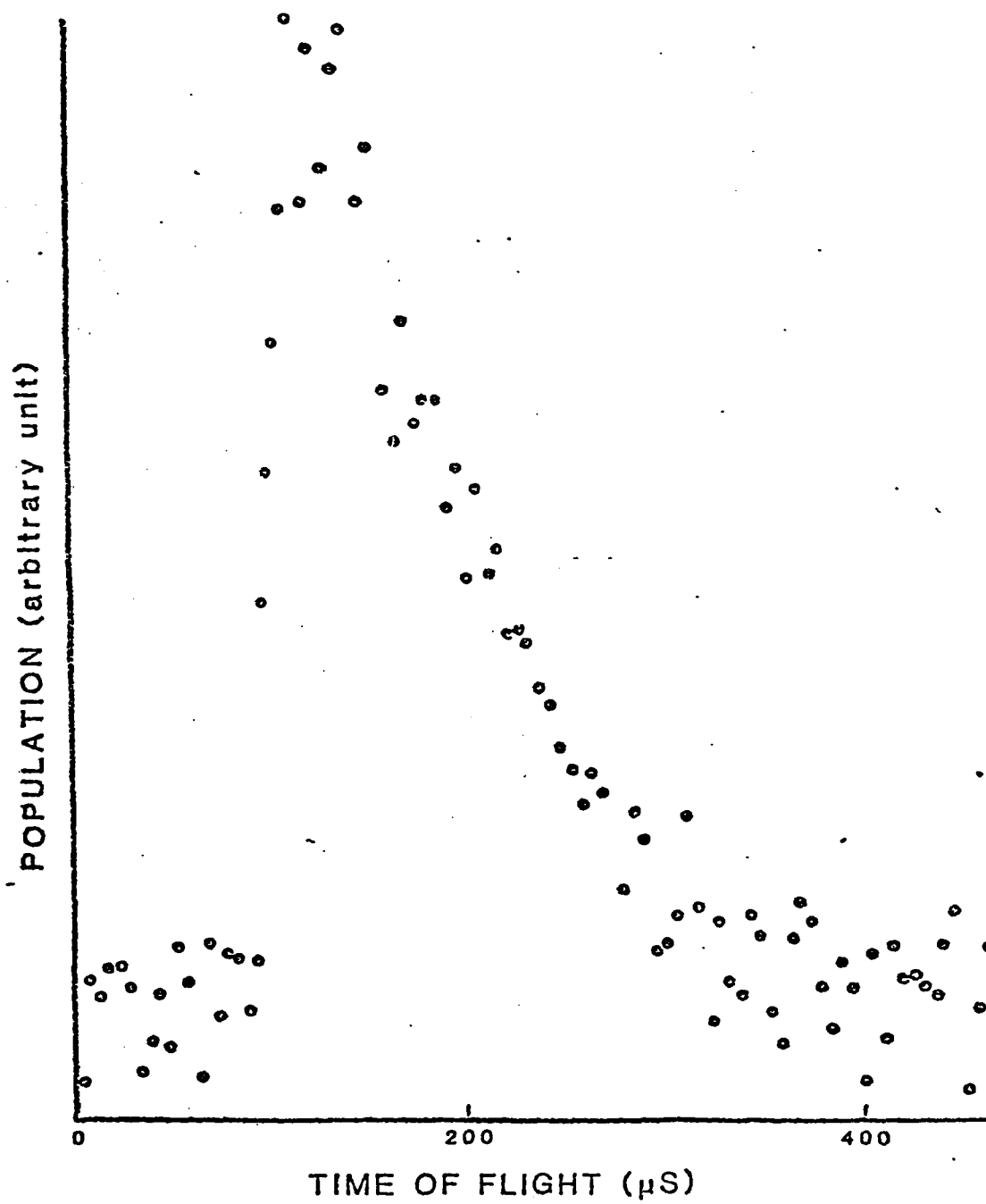
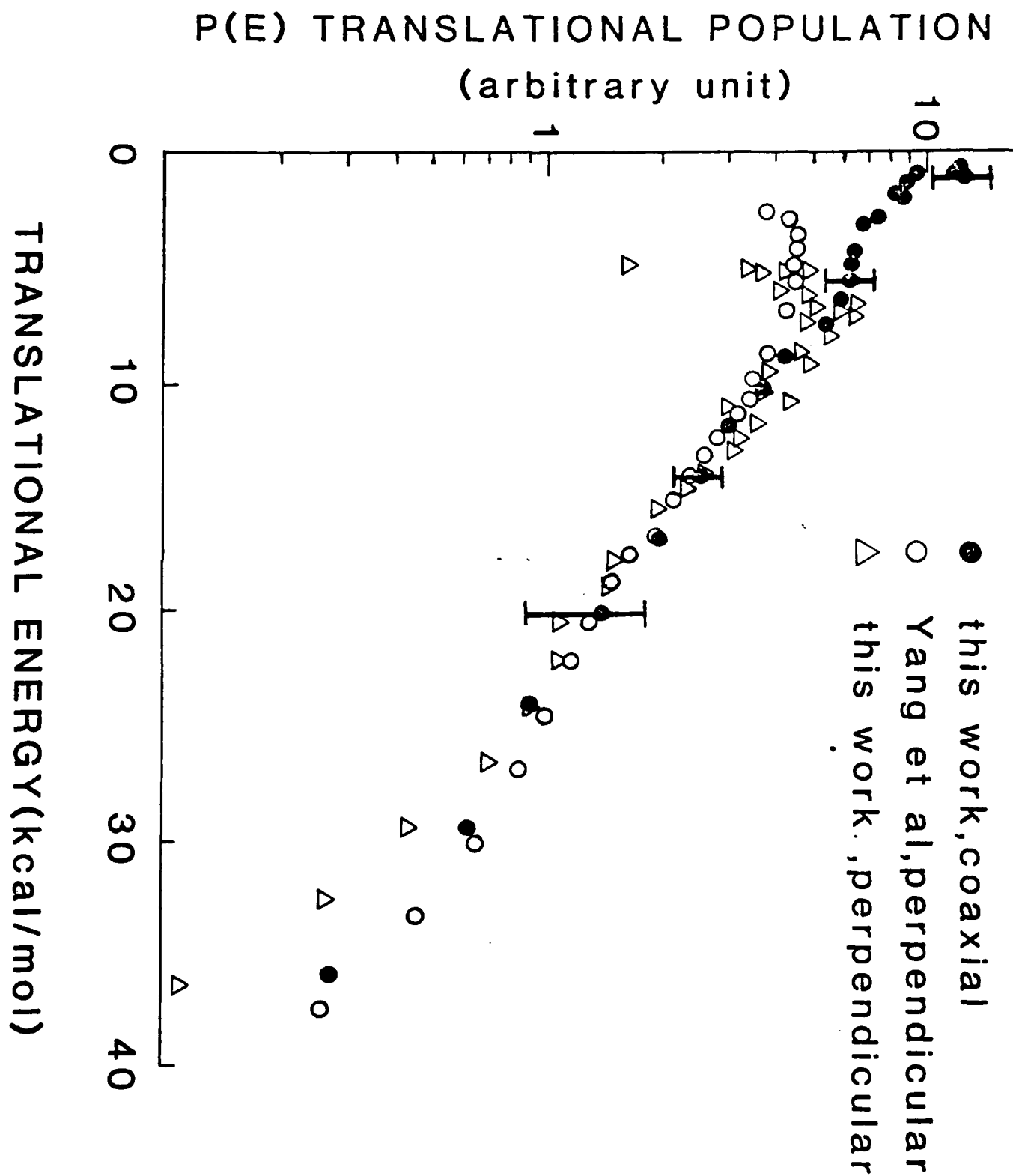


FIGURE 2

FIGURE 3



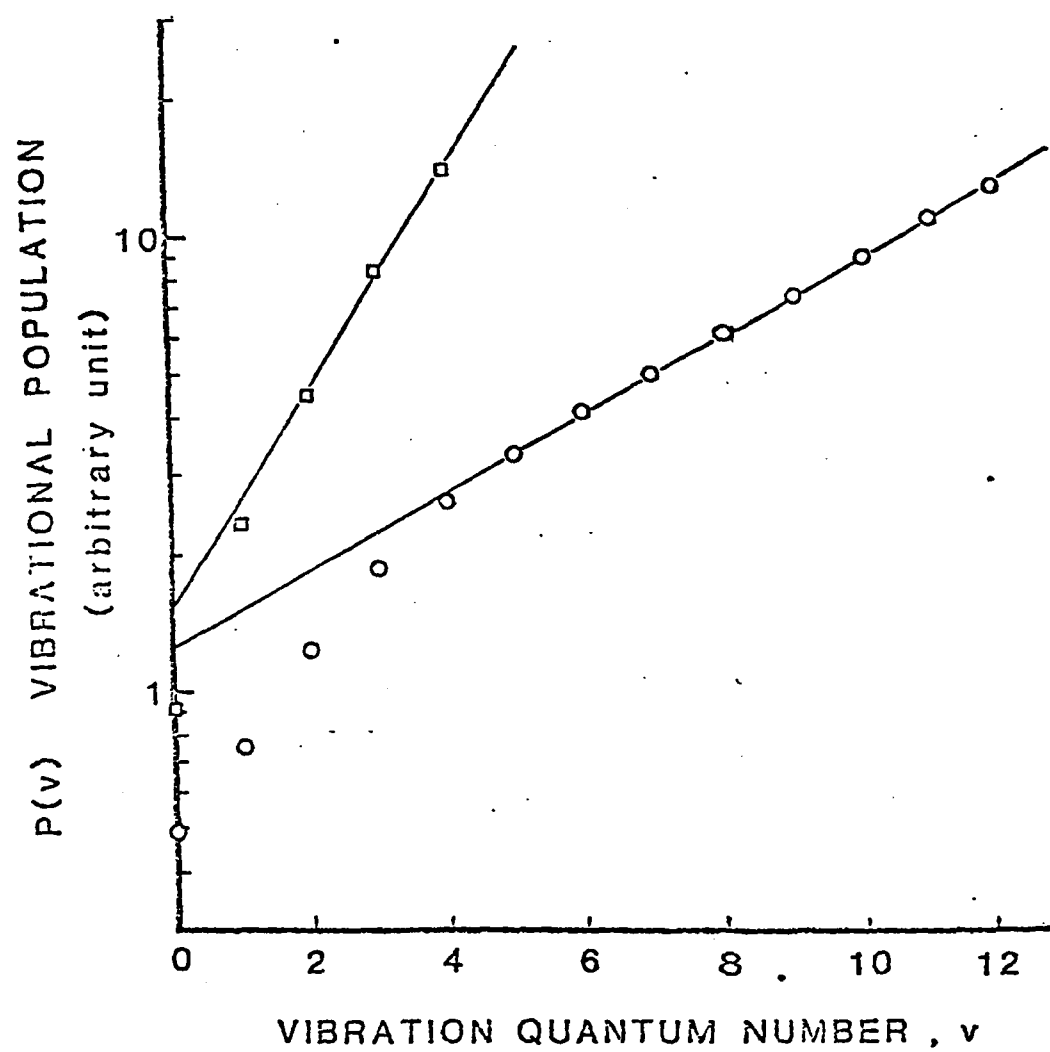


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